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AN ANTIPATHETIC RELATION BETWEEN THE HEDENBERGITE AND JOHANNSENITE COMPONENTS IN SKARN CLINOPYROXENE FROM THE KAGATA TUNGSTEN DEPOSIT, CENTRAL JAPAN

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ABSTRACT

Electron-microprobe data on clinopyroxene grains from the Kagata tungsten skarn deposit, central Japan, show that these range widely in their Mg, Mn and Fe contents (5–50 mole % of diopside, 3–18 mole % of johannsenite and 45–90 mole % of hedenbergite). Both positive and negative correlations between the Fe and Mn contents of individual grains are observed. The chemical zonation of most clinopyroxene grains is heterogeneous; however, some grains display a systematic compositional change from core to rim. The zonation pattern may be used to divide the Kagata clinopyroxene into three growth stages (I, II and III). Analysis in light of available experiments on the cation-exchange equilibrium between a Cl-bearing hydrothermal fluid and clinopyroxene suggests that (1) the mean Mg:Mn:Fe proportion in the hydrothermal fluids responsible for the formation of the clinopyroxene population is estimated to fall in a narrow range (Mg:Mn:Fe = 0.15–2.15:61–69:31–39), (2) clinopyroxene grains having a negative Fe–Mn correlation formed during the earlier stage (I to II), at a constant Mg ratio [Mg/(Mg + Mn + Fe)] in the associated fluid of around 0.2, whereas clinopyroxene with a positive Fe–Mn correlation crystallized in the later stage (II to III) during an increase of the Mg ratio in the fluid from 0.2 to 2. Systematic variations in the Mg ratio in the fluid with relatively constant Mg:Fe:Mn proportions may have produced an antipathetic relation between the hedenbergite and johannsenite components in the skarn clinopyroxene at Kagata.

Keywords: skarn, clinopyroxene, hedenbergite, johannsenite, compositional pattern, cation exchange, skarn-forming fluid, Kagata tungsten deposit, Japan.

SOMMAIRE

Un programme d'analyses à la microsonde électronique du clinopyroxène des skarns à tungstène du gisement de Kagata, dans la partie centrale du Japon, montre que ce minéral varie fortement en Mg, Mn et Fe (5–50% de diopside, 3–18% de johannsenite et 45–90% de hédenbergite, base molaire). Une corrélation soit positive, soit négative caractérise les teneurs en Fe et Mn des grains individuels. La zonation chimique de la plupart des grains est hétérogène, en général, mais dans certains cas, il y a zonation systématique du coeur vers la bordure. Cette zonation sert à diviser le clinopyroxène en trois étapes de croissance (I, II et III). Une évaluation en termes des données disponibles sur les équilibres d'échange cationique entre phase fluide chlorurée et clinopyroxène montre que 1) la proportion moyenne Mg:Mn:Fe de la phase fluide responsable de la formation du clinopyroxène à Kagata n'aurait varié que légèrement (Mg 0.15–2.15, Mn 61–69, Fe 31–39); 2) le clinopyroxène qui montre une corrélation Fe–Mn négative a cristallisé à un stade précoce (I à II) à un rapport Mg/(Mg + Mn + Fe) constant (environ 0.2) dans la phase fluide, tandis que les cristaux qui font preuve d'une corrélation positive entre Fe et Mn se sont formés à un stade ultérieur (II à III), au cours d'une augmentation dans ce même rapport dans le fluide, de 0.2 à 2. Des modifications systématiques dans le rapport Mg/(Mg + Mn + Fe) de la phase fluide en même temps qu'une proportion Mg:Fe:Mn relativement constante pourraient expliquer la variation antithétique entre hédenbergite et johannsenite dans le clinopyroxène des skarns à Kagata.

(Traduit par la Rédaction)

Mots-clés: skarn, clinopyroxène, hédenbergite, johannsenite, composition, échange cationique, phase fluide, gisement à tungstène de Kagata, Japon.

INTRODUCTION

Calcium-rich clinopyroxene is one of the most common minerals in skarn deposits. Numerous studies making use of electron-microprobe data (EPMA) have revealed that the compositions of the clinopyroxene in skarns are ternary, and can be expressed as a mixture of diopside (Di), johannsenite (Jo) and hedenbergite (Hd) components. The proportion of each component is highly variable, and depends upon such factors as the composition of the ore, and of host rocks and the mineral assemblage in which the clinopyroxene occurs (*e.g.*, Einaudi 1977, Einaudi *et al.* 1981). Abrecht (1985) and Nakano (1989) reported a positive correlation between the Hd and Jo components in clinopyroxene from skarns. Similar positive Hd–Jo correlations seem to have been recognized in clinopyroxene from other skarn deposits (Sato 1980, Ozaki & Kusachi 1981, Brown *et al.* 1985), although these authors did not pay special attention to such a systematic relationship. Observation of a negative Hd–Jo relation in clinopyroxene from skarns has yet to be reported.

Regular variations in the Mg, Mn and Fe contents in a suite of clinopyroxene compositions can provide constraints on the mechanism controlling clinopyroxene composition. Iiyama (1979, 1982) carried out exchange experiments involving three cations (Mg, Mn and Fe) between Ca-rich clinopyroxene and chloride-bearing fluid. The clinopyroxene-fluid partitioning data of Iiyama enable us to discuss compositional variations of skarn clinopyroxene in terms of the composition of the associated fluid.

Both positive and negative Hd–Jo correlations are present in skarn clinopyroxene from the Kagata tungsten deposit of central Japan. In this article, the two types of regular Hd–Jo relations developed in clinopyroxene at Kagata are described and discussed in light of Iiyama's Mg–Mn–Fe exchange experiments between clinopyroxene and hydrothermal fluid.

OUTLINE OF GEOLOGY AND SAMPLE DESCRIPTION

The Kagata deposit is located 80 km northeast of Tokyo. This tungsten-bearing skarn deposit was closed in 1957, and host-rock outcrops are only locally being developed at present. However, previous studies (Takahashi & Ueno 1960, Ikeda *et al.* 1983) have established that the surrounding lithologies consist of granodiorite, granitic pegmatite dyke, bedded chert, pelitic or psammitic hornfels and crystalline limestone. Ores and skarns are mainly located along the boundary between the crystalline limestone and the granodiorite intrusive body.

The mineralogy and mineral chemistry of magmatic–hydrothermal deposits are strongly affected by the oxidizing condition of their associated magma. According to Ishihara (1981), granitic rocks can be classified geochemically into two types, those of the magnetite series and those of the ilmenite series, the difference being attributable to the difference in oxygen fugacity during evolution of the granitic magma. Ishihara further demonstrated that most tungsten deposits in Japan are accompanied by ilmenite-series granites, which are more reduced than magnetite-series granites. An occurrence of spessartine garnet and ferrobustamite, both of which are considered as typical indicators of a reduced skarn, have been reported from the Kagata deposit (Shimazaki 1977, 1980). Kwak & White (1982) further subdivided tungsten skarn deposits into a W–F–Sn type, occurring in the reduced skarn, and a W–Mo–Cu type, in oxidized skarn. Twenty km northeast of the Kagata deposit, the Takatori vein-type deposit is a representative of the W–F–Sn type of deposit in Japan. Both Kagata and Takatori deposits are associated with the so-called Tsukuba-type granitic rocks, of the ilmenite series. These geological and geochemical observations indicate that the Kagata deposit can be grouped as a typical reduced, W–Sn–F type of deposit.

All samples were collected from old dumps. The clinopyroxene-bearing skarn is divided into four types according to its associated mineralogy; sulfide-bearing clinopyroxene skarn (sample No. 32), garnet–clinopyroxene skarn (25 and 35), plagioclase–clinopyroxene skarn (sample 22) and barren clinopyroxene skarn (1 and 31). The clinopyroxene shows a slight variation in crystal habit from equigranular to long prismatic, and the grain size varies from 10 mm to a few mm. Scheelite is present as sporadic disseminations in the clinopyroxene. Garnet contains clinopyroxene inclusions and also may replace the clinopyroxene. Calcite or quartz (or both) occurs as interstitial infillings or as veinlets in the skarn minerals. The sulfides, mainly composed of pyrrhotite, pyrite and chalcopyrite, are present as disseminations or veins in the skarn. These occurrences suggest that sulfides, quartz and calcite crystallized after the formation of clinopyroxene.

MINERAL CHEMISTRY OF CLINOPYROXENE

Analytical methods

The composition of clinopyroxene at Kagata was investigated by means of JEOL–50A and JEOL–8621 electron microprobes at the Chemical Analysis Center, University of Tsukuba. Analytical conditions were 15 kV accelerating voltage, 17.5 nA sample current and 30-second counting time per element. Most analyses were carried out on grains randomly selected on polished thin sections. Detailed analyses were performed on selected grains to document internal compositional variations.

Bulk Mg–Mn–Fe ratio of the clinopyroxene

Representative analytical data on clinopyroxene are given in Table 1. Of the eleven elements investigated (Al, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, Si and Ti), Na and Al contents were found to be present at minor levels (<0.5 wt. % Na_2O and Al_2O_3) and Cr, K and Ti were consistently present in traces, below 0.05 wt.% (expressed as oxides). The cation proportions of Na, Al, Si and Ca calculated on the basis of 6 oxygen atoms are 0.01–0.03, 0.01–0.05, 1.95–2.01 and 0.94–1.01, respectively. These values indicate that the compositions of the suite of clinopyroxene are

TABLE 1. REPRESENTATIVE ANALYTICAL DATA FOR CLINOPYROXENE FROM THE KAGATA TUNGSTEN SKARN DEPOSIT

Sample name	22 (a)	22 (b)	22 (c)	22 (d)	31 (a)	31 (b)
SiO_2	50.7	50.8	49.4	48.5	47.8	47.6
Al_2O_3	0.34	0.38	0.37	0.31	0.13	0.24
FeO*	15.5	18.5	22.5	25.3	26.3	24.6
MnO	1.47	1.63	2.27	2.45	2.40	3.72
MgO	8.01	5.89	3.19	1.31	0.49	0.66
CaO	23.1	23.1	22.2	22.0	22.5	22.6
Na_2O	0.36	0.34	0.30	0.35	0.14	0.22
Total	99.49	100.64	100.23	100.22	99.76	99.64
			on the basis of 6 oxygen			
Si	1.985	1.992	1.989	1.984	1.980	1.973
Al	0.016	0.018	0.018	0.015	0.006	0.012
Fe	0.508	0.607	0.758	0.866	0.911	0.853
Mn	0.049	0.054	0.077	0.085	0.084	0.131
Mg	0.468	0.344	0.191	0.080	0.030	0.041
Ca	0.969	0.971	0.958	0.964	0.999	1.004
Na	0.027	0.026	0.023	0.028	0.011	0.018
Total	4.021	4.012	4.014	4.022	4.022	4.030

Compositions given in wt. %. * Total Fe calculated as FeO.

reasonably well expressed by the components diopside, johannsenite and hedenbergite. The data used in this study contain total cations in the range 3.985-4.030.

Statistical analysis of correlation coefficient between pairs of elements shows that a significant correlation (correlation coefficient > 0.7 or < -0.7) is observed only in three pairs, Mg-Fe, Mg-Mn and Fe-Mn. The mean composition of the clinopyroxene in some samples is presented in Table 2. In spite of a broad compositional variation in each sample and a different mean composition for each, a majority of the clinopyroxene compositions is found to fall in a relatively narrow range: 5-15 mole % Jo and 80-90 mole % Hd. These compositional ranges are consistent with those of clinopyroxene from other pyrometasomatic W-Sn-F deposits in Japan, such as the Fujigatani mine (Sato 1980) and the Kiwada mine (Fujii 1980). The compositional similarity of garnet from these deposits has already been noted (Shimazaki 1977, Sato 1980). Similar geological environments may possibly be reflected by the chemistry of garnet or clinopyroxene (Shimazaki 1980).

TABLE 2. MEAN PROPORTION OF Hd, Jo AND Di (%) IN THE CLINOPYROXENE AND OF Fe, Mn AND Mg (%) IN THE ASSOCIATED FLUID

Sample	22	1	25	31	32	35
			(clinopyroxene)			
Hd	57.8	82.7	88.3	85.0	84.6	85.6
Jo	5.23	8.41	7.77	10.9	8.19	9.78
Di	37.0	8.59	3.93	4.10	7.21	4.62
			(fluid)			
Fe	67.4	66.1	69.3	60.8	67.2	63.5
Mn	30.5	33.6	30.5	39.0	32.5	36.3
Mg	2.15	0.36	0.15	0.15	0.29	0.17

Clinopyroxene displaying negative correlations between hedenbergite and johannsenite

A majority of clinopyroxene samples show a distinct relation between their Fe and Mn contents. Most samples, except sample 22, are composed of clinopyroxene that displays a negative Hd-Jo relation; that is, the johannsenite component decreases with an increase in the hedenbergite component (Fig. 1). The relations noted in this figure were deduced by plotting compositions of clinopyroxene grains randomly selected on a polished thin section of each sample. Although a similar negative Hd-Jo correlation is observed in samples 1, 25, 31, 32 and 35, their mean composition differs slightly from sample to sample (Table 2).

Individual grains within a single sample also display the same negative Hd-Jo relation. Figure 2 displays a compositional pattern for an aggregate of four clinopyroxene grains in sample 1. It is evident from this figure that all grains have a higher level of Jo and Di components in the core than in the rim. Figure 3 shows the compositional variation of three clinopyroxene grains arbitrarily selected on a thin section of the same sample. Although the Hd proportions of this clinopyroxene grain vary continuously from 72 to 90 mole % on this figure, a majority also plot around 80-90 mole %. The composition of clinopyroxene grains randomly selected on a thin section of this sample is also plotted on the Hd-Jo diagram (All in Fig. 3). The compositional similarity between single grains (A, B and C in Fig. 3) and total clinopyroxene grains (All) in the thin section suggests that most grains were formed contemporaneously. Considering that this sample is entirely composed of clinopyroxene with local infilling of quartz in the later stage, the low Jo component in the rim part was certainly formed during the clinopyroxene growth rather than by later alteration along grain boundaries.

Clinopyroxene displaying positive correlations between hedenbergite and johannsenite

The clinopyroxene in sample 22 has a range of compositions quite different from others analyzed in this study (Fig. 1). The skarn from which sample 22 was collected is mainly composed of clinopyroxene, quartz, plagioclase, pyrrhotite, pyrite, chalcopyrite and small amounts of sphalerite. Clinopyroxene grains are dispersed in, or are partly replaced by, quartz and sulfides. The presence of plagioclase $An_{35\pm6}$ is characteristic of this skarn. Some grains are coarse (0.01-0.1 mm) and show albite twins, but others are brecciated and broken into several pieces. These textural and composition-

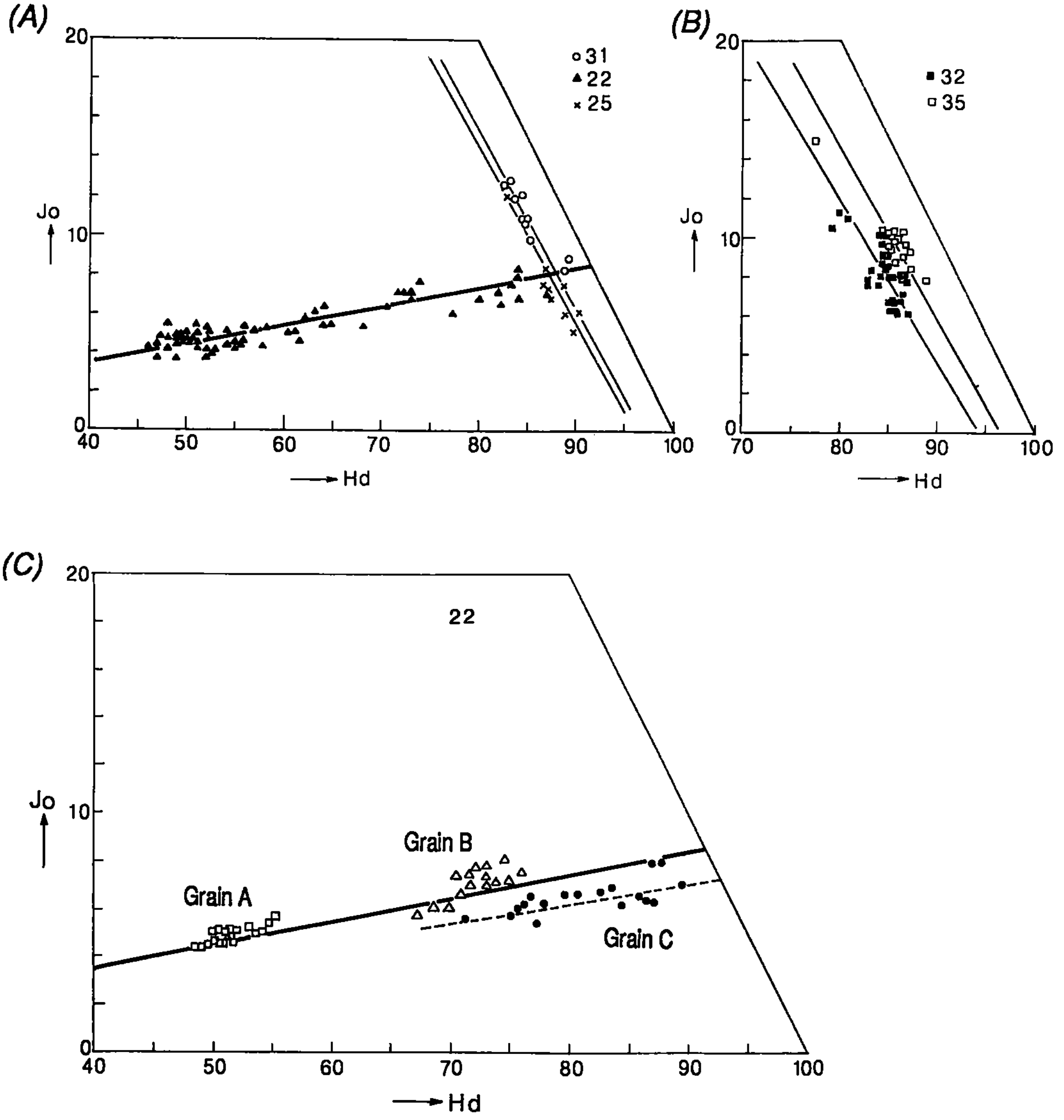
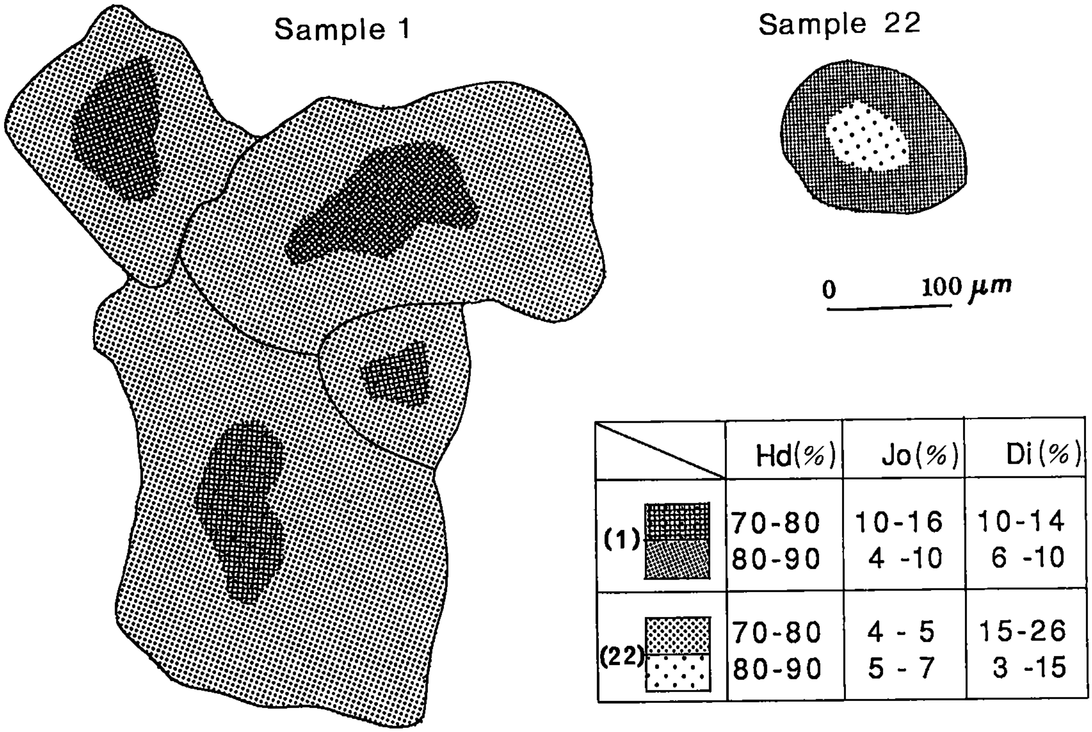


FIG. 1. Plot of clinopyroxene composition on hedenbergite (Hd) – johannsenite (Jo) diagram. Sample numbers are the same as Table 1.

al features of plagioclase seem to suggest that the original rock of this skarn was granitic, whereas those of the samples displaying the negative Hd–Jo correlation seem to indicate crystalline limestone as a precursor.

Chemical compositions of clinopyroxene grains randomly selected on a polished thin section of this sample (Fig. 1A) vary continuously over a wide range (Di_{2-52}, Jo_{3-8}, Hd_{45-90}), although most grains fall in a limited region around Hd_{45-65} and Jo_{4-6} on this diagram. The mineral chemistry of this clinopyroxene is documented in Table 1. A distinct positive correlation is apparent between the Fe and the Mn contents of clinopyroxene grains (positive Hd–Jo relation represented as a thick line in Fig. 1). It is also notable that each component is not uniformly distributed on this diagram. For example, high levels of the Hd component are mostly distributed in low-Hd portions.

Although there are no grains whose compositions cover the whole range analyzed in this sample, a similar positive Hd–Jo relation is observed in



	Hd(%)	Jo(%)	Di(%)
(1) ▦	70-80	10-16	10-14
(1) ▩	80-90	4 -10	6 -10
(22) ░	70-80	4 - 5	15-26
(22) ⁚	80-90	5 - 7	3 -15

FIG. 2. Compositional map of clinopyroxene grains. Levels of Hd, Jo and Di components are expressed in mole %.

single grains (Fig. 1C). The Jo contents of grain C are a little lower than those of clinopyroxene on the thick line. Thus, the compositional range is not identical in different grains. However, there exists a positive Hd–Jo relation within each grain. Clinopyroxene grains of different compositional range cannot be distinguished microscopically. In spite of the distinct correlation between the Fe and Mn contents, the compositional pattern within a single clinopyroxene grain is not always uniform. The compositional pattern of clinopyroxene grain in sample 22 (grain C in Fig. 1C) is shown in Figure 2. Grain C shows a gradual decrease in Fe content from the core (Hd_{90}) to the rim (Hd_{70}), whereas grains having a composition about Hd_{50-70} do not show any systematic compositional trend from the core to the rim.

Growth stages of clinopyroxene

The two distinct compositional patterns in clinopyroxene grains from Kagata (Fig. 2) provide

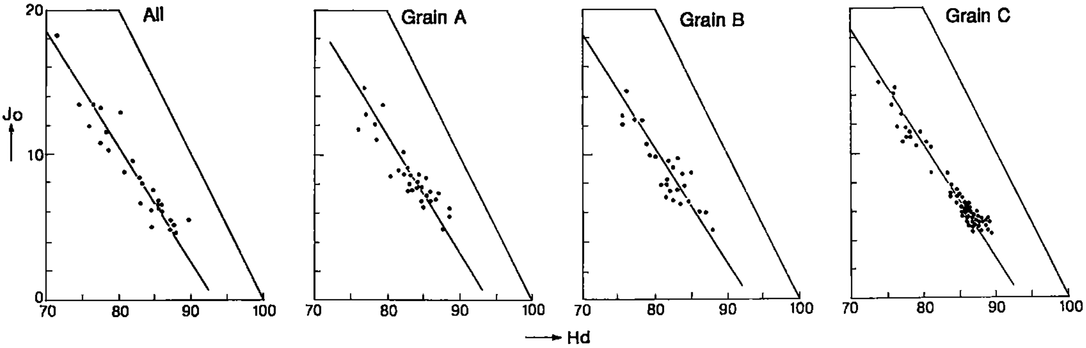


FIG. 3. Plot of clinopyroxene compositions in sample 1 on hedenbergite (Hd) – johannsenite (Jo) diagram.

a basis of recognition of three growth stages (I, II, III). It is also notable that the rim part of clinopyroxene with a negative Hd–Jo correlation corresponds in composition to the core part of clinopyroxene grains having a positive Hd–Jo correlation. This suggests that the former clinopyroxene was formed in the earlier stage from I to II, whereas the later clinopyroxene crystallized at a later stage, from II to III; that is, stage-I clinopyroxene is characterized by high Mn contents (Di_{10-14}, Jo_{10-16}, Hd_{65-75}), stage-II clinopyroxene, by high Fe contents (Di_{6-10}, Jo_{4-11}, Hd_{80-90}), and stage-III clinopyroxene, by high Mg contents (Di_{31-49}, Jo_{4-6}, Hd_{45-65}).

RELATION OF Fe:Mn:Mg PROPORTION BETWEEN CLINOPYROXENE AND HYDROTHERMAL FLUID

Mean Fe:Mn:Mg proportion in the associated hydrothermal fluids

The Kagata suite of clinopyroxene was probably formed from a metasomatic hydrothermal fluid developed in the so-called Tsukuba-type granitic rocks. If surface equilibrium between the clinopyroxene and hydrothermal fluid was attained, Mg:Mn:Fe proportions in the hydrothermal fluid can be estimated by utilizing the partitioning of Mg, Mn and Fe between clinopyroxene and hydrothermal fluid. Iiyama (1979, 1982) studied the cation-exchange equilibrium between clinopyroxene and fluid for Mn–Mg, Mn–Fe and Fe–Mg pairs at 600°C and 1 kbar. The partition relations among the three pairs are given by the following equations:

$$(Mn/Mg)_{cpx} = K_1 \times (Mn/Mg)_{fluid} \quad (1)$$
$$(Mn/Fe)_{cpx} = K_2 \times (Mn/Fe)_{fluid} \quad (2)$$
$$(Fe/Mg)_{cpx} = K_3 \times (Fe/Mg)_{fluid} \quad (3)$$

where cpx and fluid denote a clinopyroxene and a hydrothermal fluid, respectively, and K_1, K_2 and K_3 are the distribution coefficients. It is assumed from Iiyama's equilibrium isotherms that K_1, K_2 and K_3 have a constant value of 0.01, 0.05 and 0.2, respectively (Nakano 1989).

By using these values, the mean value of the Mg, Mn and Fe fraction of clinopyroxene for each sample can be recalculated in terms of those of fluids (Table 2). The result of calculation shows that the mean Mg, Mn and Fe proportions are similar for all samples, 0.15–2.15% for Mg, 30–40% for Mn and 60–70% for Fe. Thus, the hydrothermal fluid responsible for clinopyroxene deposition at Kagata is found to be as a whole relatively homogeneous, at least with respect to levels of Mg, Mn and Fe. This original Mg:Mn:Fe proportion for the Kagata skarn-forming fluid is not unrealistic. For example, Muffler & White (1969) reported a geothermal brine in the Salton Sea geothermal area with a proportion of Mg:Mn:Fe of 1.4:37.4:61.2, which is quite similar to that proposed for the skarn-forming fluid at Kagata.

It is also possible, by changing the Mg:Mn:Fe proportion in the fluid, to trace the Di–Jo–Hd relation of clinopyroxene and to simulate the antipathetic regular Hd–Jo relation. Nakano (1989) proposed a "fluctuation model" to explain the variable compositional pattern in the skarn clinopyroxene. This model seems to partly succeed in explaining the clinopyroxene compositions heterogeneously developed on the scale of a thin section. According to this model, clinopyroxene compositions formed from relatively homogeneous fluids, which experienced local variations in their Mg:Mn:Fe proportion instead of from successively different compositions. However, some clinopyroxene grains that display a systematic change in composition from their core to their rim cannot be explained by such a model only.

REGULAR HD–JO RELATION DUE TO VARIATION OF Fe:Mn:Mg PROPORTION IN THE HYDROTHERMAL FLUID

To determine how the Fe:Mn:Mg proportion of a clinopyroxene changes with that of hydrothermal fluid, two cases were considered. In case 1, the ratio of one element to the sum of the three elements (Fe, Mn and Mg) in the fluid changes while the ratio between the other two elements is kept constant. In case 2, the ratio of one element in the fluid is kept constant while the ratio between the other two elements in the fluid is allowed to change. Four cases are shown in Figure 4. The detailed relations also are shown in Figure 4 for a restricted compositional range corresponding to that of the Kagata example.

The negative Hd–Jo relation occurs in the three cases. In the first case, the Mg fraction in the fluid is kept constant while the Fe and Mn fractions in the fluid change mutually. This case is fairly consistent with the negative Hd–Jo relation in clinopyroxene at Kagata. In the second case, Fe/(Fe+Mn+Mg) in the fluid changes while the Mn/Mg ratio remains constant. In the third case, the Mn fraction in the fluid changes while the Fe/Mg ratio remains constant. However, the last two cases deviate from the Hd–Jo relation displayed at Kagata.

On the other hand, the positive Hd–Jo relation occurs in the case where the Mg fraction in the fluid changes at the constant Fe/Mn ratio. It also

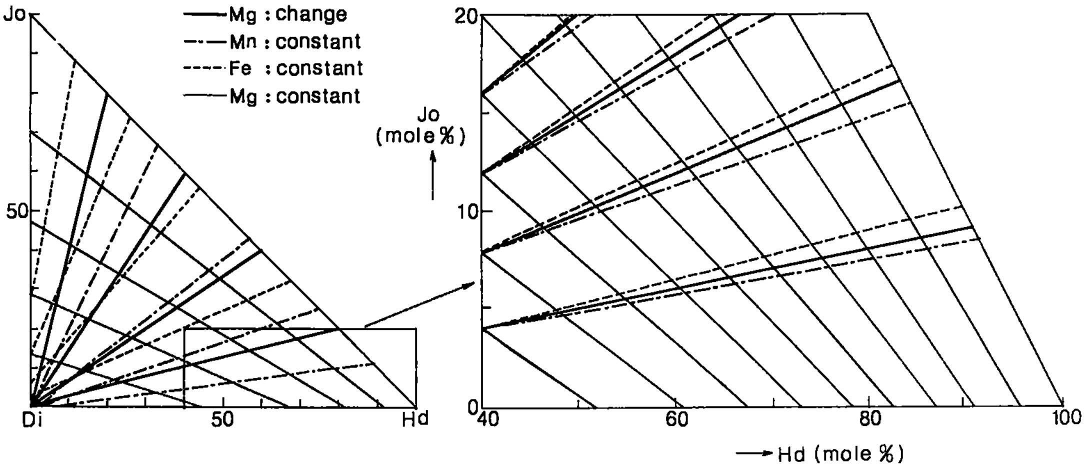


FIG. 4. Diagram showing the variation of clinopyroxene composition in accordance with that of its associated fluid composition. See the text for details.

occurs in the case where the Fe or Mn fraction in the fluid is kept constant. As the latter two cases correspond to changes in the Mn/Mg or Fe/Mg ratio of the fluid, respectively, the positive Hd–Jo relation appears to occur only for the case in which the Mg fraction in the fluid changes. These three cases show a similar inclination of lines on the Hd–Jo diagram in the observed compositional range for clinopyroxene compositions at Kagata (Fig. 4).

The thin lines that show the negative Hd–Jo relation in Figure 1 depict the case in which only the Fe/Mn ratio of the hydrothermal fluid successively changes the mean composition of clinopyroxene in each sample. The thick lines, which show the positive Hd–Jo relation in Figure 1, depict the case in which only the Mg fraction in the fluid successively changes the mean composition of sample 22. It is notable that the line for each sample in this diagram is consistent with the Hd–Jo relation of clinopyroxenes at Kagata. This seems to support the hypothesis that a wide variety of clinopyroxene compositions is affected significantly by the Mg content of the fluid and its behavior as the fluid evolves.

The temperature of formation of the skarn clinopyroxene is generally assumed to be around 300–500°C (*e.g.*, Shimazaki *et al.* 1986), which is slightly lower than the temperature (600°C) at which the partition experiments were carried out. Nevertheless, the small departure of partition coefficients as a function of temperature is unlikely to modify the above conclusion.

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